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Polyaniline and Carbon Nanotubes Based Composites Containing Whole Units and Fragments of Nanotubes

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Using surface-enhanced Raman scattering (SERS) and Fourier transform infrared (FTIR) spectroscopy, we show that composites based on polyaniline (PANI) and single-walled carbon nanotubes (SWNTs) are different when they are prepared by two different methods: (1) by adding dispersed SWNTs to the polymer solutions and (2) by chemical polymerization of aniline in the presence of SWNTs. The difference originates from the irreversible chemical transformation of SWNTs in the polymerization medium. The synthesis medium used for the preparation of PANI transforms SWNTs into fragments of shorter length like closed-shell fullerenes. This explains the similarity of SERS and FTIR spectra of the composites PANI/SWNTs and PANI/C_{60} chemically prepared. All compounds exhibit an absorption band at 1144 cm^{-1} in their FTIR spectra, increasing with the carbon nanoparticules content, as a signature of a charge transfer between the constituents. Besides, the FTIR spectrum of the compounds obtained by adding SWNTs to the polymer solution display an intense absorption band with two components at 773 and 755 cm^{-1}, which are associated with the vibration of deformation of the benzene and the quinoid ring, respectively. This indicates a strong hindrance effect produced by the binding on the polymer chain of voluminous carbon particles as nanotubes and large fragments of nanotubes.

1. Introduction

Conducting polymers, fullerenes, and carbon nanotubes (CNTs) are among the main components providing a new class of carbon-based advanced materials. As a general rule, two methods are used to prepare these composites: one consists of direct mixing of compounds, and the other is by chemical synthesis. The former procedure can lead to a doping process as observed generally by mixing a polymer and a doping agent. The latter consists of a chemical or electrochemical polymerization of the monomer with addition of carbon nanoparticles as a supplementary reactive agent. In both cases, the final product is a composite of increased conductivity, as reported previously for composites such as polypyrrole/ SWNTs[1,2] and PANI/multiwalled carbon nanotubes (MWNTs).[3,4] A priori, both preparation methods have led to similar compounds if one supposes that the polymerization process occurs without damaging the added carbon nanoparticles. The assumption is true only for C_{60}, whereas in the case of single-walled carbon nanotubes (SWNTs) some reaction takes place with the synthesis medium. In this respect, the sulfuric acid is highly reactive, transforming SWNTs in other graphite particles, as observed in highly oriented pyrolytic graphite (HOPG), closed-shell fullerenes, and even amorphous carbon.[5] Besides, the addition of $K_2Cr_2O_7$ increases the oxidation power of the synthesis medium, leading to a supplementary chemical transformation of CNTs.[5]

Both composites (i.e., prepared by the two methods described above) exhibit an increase of conductivity, which will be studied later. The primary aim of this work was to show the differences that appear when composites PANI/SWNTs are prepared on one hand by chemical polymerization of aniline in the presence of SWNTs, and on the other hand by the addition of SWNTs to the polymer solution.

Polyaniline (PANI) is a suitable material to demonstrate the chemical transformation of CNTs occurring in the preparation processes of the PANI/SWNTs composite. As a matter of fact, by the existence of two entities—reduced and oxidized—in the repeating unit of the emeraldine base, one can better illustrate the interaction with the carbon nanoparticles.

To do so, vibrational spectroscopies of such polymers, depending on their structure and doping state, are

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relevant techniques. More particularly, Raman and FTIR spectra turn out to be a very informative. In addition, the possibility of observing individual tubes dispersed in the polymer matrix is of great interest. Furthermore, to identify the intrinsic properties of the transformed tubes, it is also needed to carry out Raman studies on nanotubes in low concentration and this is why we used surface-enhanced Raman scattering (SERS) as an appropriate tool, as it operates with enhanced Raman signals.

2. Experimental Section

2.1 Preparation of Emeraldine Base. Polyaniline (PANI) was synthesized by chemical polymerization of aniline[6] using reagents of synthetic grade (Merck). In a typical procedure, two solutions of aniline (1.022 g, 1.09 10^{-2} mol) in 25 mL of 2 M H_2SO_4 and $K_2Cr_2O_7$ (0.56 g, 1.9 10^{-3} mol) in 25 mL of 2 M H_2SO_4 were mixed together and left standing under ultrasonics for 2 h at 0 °C. The resulting green suspension, indicating the formation of polyaniline in its emeraldine salt form (PANI-ES), was then filtered, and the filter cake was washed with 1000 mL of deionized water. The filter cake was then stirred in ammonium hydroxide solution (500 mL, 1 M NH_4OH) for 1 h to transform the salt form (PANI-ES) into the base one (PANI-EB). After filtering, the oligomers were extracted with 400 mL of acetonitrile (CH_3CN) until the solvent was colorless and the remaining powder was totally dried under vacuum at room temperature. Finally, 0.35 g of PANI-EB powder was collected, corresponding to ca. 35% reaction yield with respect to the aniline substrate.

We studied two types of PANI/SWNTs composites, labeled M and S. In both cases, we used single-walled carbon nanotubes produced and purified in the Groupe de Dynamique des Phases Condensées at the University of Montpellier.[7]

2.2 Preparation of the PANI/SWNT Composites from M and S Series. Composites of the M series were prepared by mixing PANI-EB dissolved in *N*-methyl-2-pyrrolidinone (NMP) with an appropriate amount of SWNTs, followed by careful solvent evaporation. In particular, M_1, M_2, and M_3 composites were obtained by adding 6, 2, and 0.6 mg, respectively, of SWNTs to 1 mL of 0.2 wt % solution of PANI-EB in NMP. The mixtures were prepared several days in advance and were ultrasonically homogenized for ca. 30 min immediately before the film preparation. Assuming that the density of the polymer solution is 1 g/cm^3 (which is a reasonable assumption taking into account the density of the solvent (1.033 g/ cm^3) and the low concentration of the polymer), the mass ratio of PANI-EB/ SWNTs in M_1, M_2, and M_3 composites was 3.33, 1, and 0.33, respectively. The M composites, investigated by SERS and FTIR spectroscopy, were prepared in films deposited on metallic (Au and Ag) and KBr substrates, respectively.

For the preparation of the composites of the S series, a similar aniline polymerization procedure was applied, i.e., an oxidative polymerization of the monomer followed by the deprotonation of the obtained PANI-ES to give PANI-EB. The removal of the oligomers was done by extraction with acetonitrile. The only difference was that, 5 min after starting the polymerization, different masses of SWNTs were added to the reaction mixture: 10, 60, and 120 mg in the case of S_1, S_2, and S_3 composites, respectively. Assuming that the whole quantity of nanotubes is maintained in the final products, the PANI/SWNTs mass ratios in the S series composites were calculated on the basis of the experimentally determined reaction yield. In particular, in the first preparation 575 mg of the S_1 composite was obtained, which consisted of 10 mg of SWNTs and 565 mg of the polymer, giving the PANI-EB/SWNTs mass ratio of 56.5. The preparation of S_2 yielded 614 mg of the product (554 mg of the polymer and 60 mg of SWNTs) which corresponds to the PANI-EB/SWNTs mass ratio of 9.2. The same calculations lead to the following composition of S_3: mass of the product 653 mg (533 mg of the polymer and 120 mg of SWNTs), which gives a PANI-EB/SWNT mass ratio of 4.4. We notice that composites of the S series are very sensitive to the quantity of nanotubes added to the polymerization mixture, as the use of SWNTs quantities the same as those for the M series would lead to compounds nearly identical. This is illustrated by a SERS spectra similar to that of the S_3 composite. However, to show the role of the concentration of carbon nanotubes in the case of the composites of the S series, we have selected for these compounds greater PANI-EB/SWNTs mass ratios.

S composites are powders in their final morphological form. For SERS and FTIR measurements, films were prepared from solution of the S composite of a 0.2 wt % concentration in NMP and deposited on metallic (Ag, Au) or KBr substrate by evaporation of the solvent.

2.3 SERS and FTIR Measurements. SERS spectra were recorded in a backscattering geometry with the 1064 nm excitation wavelength using a FT Raman Bruker RFS 100 spectrophotometer. For SERS measurements, films used were of ~150 nm thickness deposited on Au and Ag substrates with a rough microstructure in the range of 10−100 nm.[8] Films were obtained by the procedure described above.

FTIR spectra, in the range 400−4000 cm^{-1} with a 4 cm^{-1} resolution, were obtained on films deposited also by evaporation of the solvent on KBr windows, using a Bruker IFS 28 spectrophotometer. All spectra were recorded at room temperature in ambient air.

3. Results and Discussion

3.1 SERS Spectroscopy Studies on SWNTs−Anilinium Bisulfate Mixture. Although the same concentration of monomer and oxidizing agent were used for the preparation of all compounds, a greater reaction yield was always observed in the case of the composites from the S series (around 55%) than for the M series (around 35%). This difference can be interpreted in the following way.

The polymerization of aniline is controlled by the relationship between the monomer and the oxidizing agent defined by the *K* parameter[9]

$$K = \frac{2.5n_{\mathrm{an}}}{n_{\mathrm{ox}}n_{\mathrm{e}}} \tag{1}$$

in which n_{an} and n_{ox} are the number of moles of aniline and oxidizing agent, respectively; n_{e} is the number of electrons necessary to reduce one molecule of the oxidizing agent; and 2.5 is the average number of electrons necessary for the oxidation of an aniline mole to polyemeraldine. By decreasing the value of *K* parameter, one increases the polymerization reaction yield[10] and this can be achieved either by increasing the concentration of the oxidation agent in relation to the monomer concentration or by reducing the aniline concentration against the concentration of oxidizing agent.

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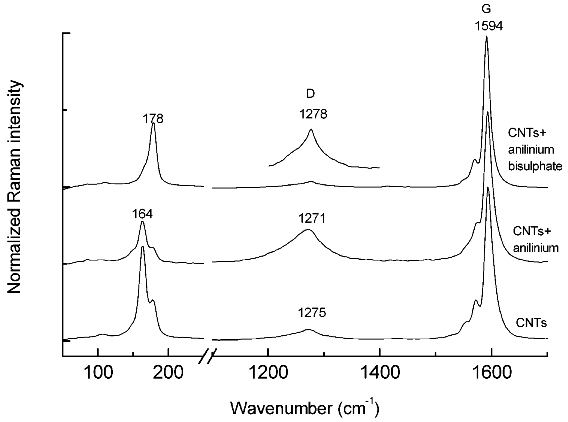
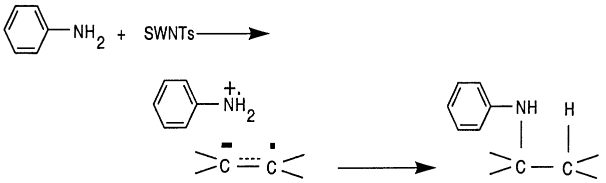


Figure 1. Evidence by SERS spectroscopy of the reaction of carbon nanotubes with aniline (curve 2) and anilinium bisulfate (curve 3). Curve 1 corresponds to the SWNTs in films.

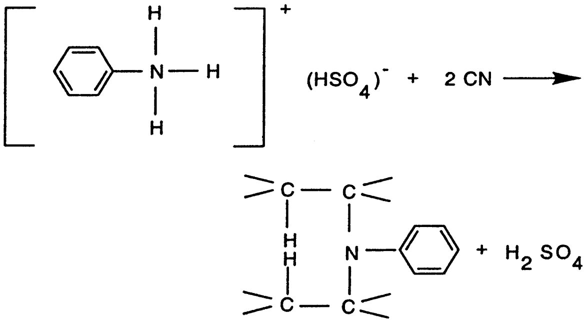
It is known that aniline reacting with carbon nanotubes or fullerenes forms charge-transfer complexes as shown below,[11] followed by its addition to the double bond:



(2)

This type of reaction is evidenced by SERS studies performed at 1064 nm laser excitation on an aniline–carbon nanotubes mixture of 6.4 mg of SWNTs added to 0.8 mL of aniline. Films of about 150 nm thickness were deposited on rough Au substrate. Comparison with the SERS spectrum of SWNTs alone reveals significant modifications due to the interaction with aniline. These are evident on spectrum 2 in Figure 1 by (i) the decrease of the relative intensity of the bands group in the range 100–200 cm^{-1} associated to radial breathing modes (RBM)[12] which indicates a transformation of the nanotubes; and (ii) the change in the intensity ratio between bands peaking close to 1275 and 1594 cm^{-1}, associated with disorder in the graphite lattice or defects in nanotube and in-plane stretching E_{2g} vibration mode, respectively.[13,14] This clearly shows that the interaction with aniline induces more defects on the carbon nanotubes.

Other studies concerning the interaction of SWNTs with anilinium-bisulfate were carried out too. As described above, the films used for the SERS measurements were prepared from a mixture of 6.4 mg of SWNT added to 0.8 mL of aniline in 50 mL of 2 M H_2SO_4. In this case, the main indication regarding the transformation of CNTs by interaction with anilinium-bisulfate is given by the radial breathing modes that consist of bands at 164 and 178 cm^{-1} associated with isolated and bundled tubes, respectively.[15] The decrease, or even the disappearance, of the former and the enhancement with ca. 50% of the latter without significant modifications of the other Raman bands indicates an effect of bundling up of the carbon nanotubes. Similar studies performed on anilinium-bisulfate and C_{60} mixtures have revealed that the bundle effect is replaced in this case by an aggregation effect, shown by typical variations of the SERS spectra of C_{60}. The most relevant feature is a new band situated in the low frequencies range[16] at ca. 86 cm^{-1} which, by analogy with the Raman spectrum of the dimerized C_{60}, is attributed to the Raman-active interball vibration modes.[17,18] In this context, the interaction between anilinium-bisulfate and the carbon nanoparticles such as carbon nanotubes or fullerenes could be described by eq 3:



(3)

which illustrates a process of association of CNTs achieved with the aniline as binding agent. Besides, the organic compound resulted from reaction 3 is a tertiary amine which, as well as triphenylamine, needs another chemical polymerization procedure.[19] All these side reactions contribute to an apparent increase of the reaction yield determined on the basis of gravimetric measurements.

3.2 Vibrational Properties of the Composites. SERS spectra ($\lambda_{exc} = 1064$ nm) of the M type composite are displayed in Figure 2. At first, curves M_1, M_2, and M_3 appear like a sum of the PANI-EB and SWNTs Raman spectra, each one revealing its specific characteristics. For polyaniline, the different reducing properties of the metal substrates led to different SERS spectra on Au and Ag substrate.[20] Thus, in the SERS spectrum of the PANI-EB layered on Au support, one observes two Raman bands at ca. 1325 and 1375 cm^{-1}, which reveal a semiquinone radical structure. For nanotubes (curve 1 in Figure 2), three known Raman bands are well identified.[13,14] In the low-frequency range, <300 cm^{-1}, one finds the bands associated with the radial breathing modes (RBM). The intensity and peak position of these bands, related to the tube diameter through the relation ν (cm^{-1}) = 223.75/d

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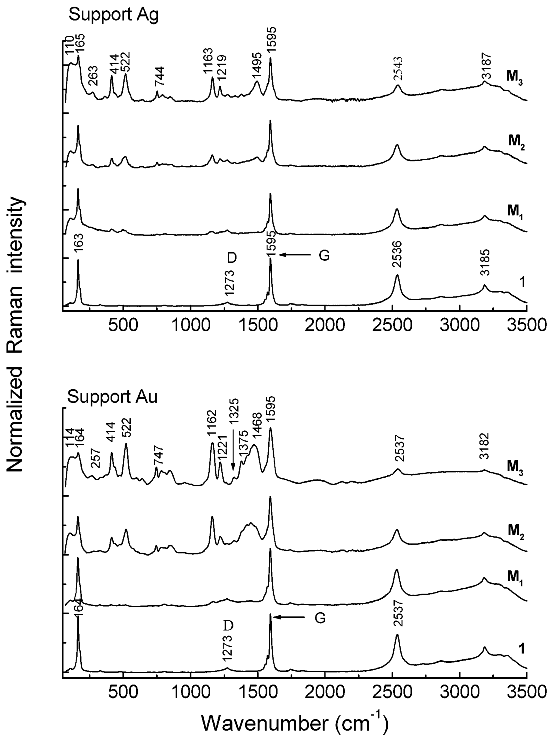

Figure 2. SERS spectra, at λ_{exc} = 1064 nm, of PANI-EB/SWNTs composites provided by mixing of PANI-EB and CNTs. M_3, M_2, and M_1 spectra correspond to the compounds with a PANI-EB/SWNT mass ratios of 3.33, 1, and 0.33, respectively. Spectrum 1 belongs to SWNTs.

(nm),[21] are very sensitive to the excitation wavelength. The strongest band at ≈164 cm^{-1} indicates that the resonance occurs over a narrow range of diameters around 1.36 nm, identified with transitions $E_{22}{}^{S}$ for semiconducting tubes.[12] The second group, consisting of the G and D bands, is found in the interval from 1100 to 1700 cm^{-1}. Both bands are not only related to the nanotubes structure: the former, peaked at ~1595 cm^{-1} attributed to in-plan stretching E_{2g} vibration mode, is also present in the Raman spectrum of other graphitic materials, like in HOPG.[13] Regarding the D band, it is considered as an indication of disorder in the graphite lattice or defects in nanotubes.[13,14] The third group, situated at ~1700−3500 cm^{-1} corresponds to the second-order Raman spectrum. As a rule, the most intense bands are those detected at approximately twice the frequency of the D and G bands i.e., at ca. 2536 and 3182 cm^{-1}. An increased disorder or more defects in the nanotube structure determines opposite variations of the D band and its second-order counterpart. Thus, the relative decrease of the second-order of D band from Figure 2 indicates a less perfect structure for the nanotubes embedded in, or bound to, the polymer. Formation of this complex is noticed in the Raman spectrum by the decrease of the RBM bands and a G band that remains as strong as before, regardless of the weight ratio of the two components in the composite. The G band, associated with tangential vibrational modes, reveals in this case the sum of contributions coming from SWNTs, nanotubes fragments, and polymer/CNTs (whole units and fragments) composites.

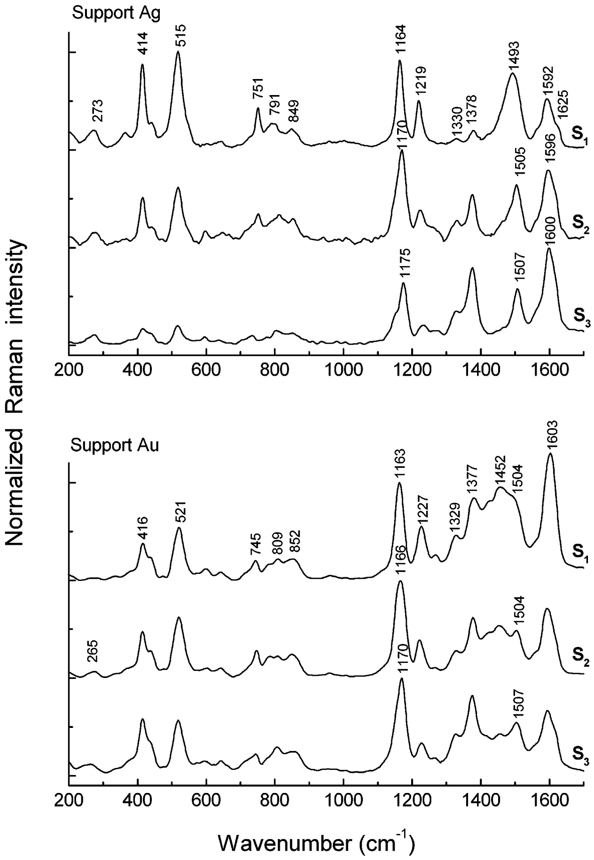

Figure 3. SERS spectra, at λ_{exc} = 1064 nm, of PANI-EB/SWNTs composites provided by chemical synthesis. S_1, S_2, and S_3 spectra correspond to the compounds with a PANI-EB/SWNTs mass ratios of 56.5, 9.2, and 4.4, respectively.

Figure 3 displays SERS spectra of composites of S type. They look like SERS spectra of fullerene-doped PANI compounds.[22] Both groups of spectra recorded on Ag and Au substrates exhibit two bands at ~1330 and ~1375 cm^{-1} that grow with the SWNTs content. This is the Raman signature of the polyaniline salt.[23] Nevertheless, the SERS spectra recorded on Ag and Au substrate exhibit some differences depending of the form of PANI. Between these, only the base form is sensitive to the type of SERS support. It is well-known that the SERS spectrum originates in two basic enhancement mechanisms: (i) electromagnetic, achieved by the resonant excitation of the surface plasmons; and (ii) chemical, mainly due to charge-transfer processes between the metallic substrate and adsorbed molecules. By using Ag or Au supports manipulated in air, we think that their different behavior is due to the interposition of an intermediate compound layer between PANI molecules and the metal substrate. Ag has a strong oxidation tendency to form a stable compound Ag_2O (ref 24) which, as a surface layer, prevents direct interaction between the polymer and the metal substrate. In this case, the SERS spectrum is similar to the regular Raman spec-

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trum recorded on PANI powder. For Au, which is the only metal that shows no direct reaction with oxygen even at high temperature,[24] the lack of a covering oxide layer permits direct interaction with the adsorbed polymer. An electron of the metal, excited by the incident photon, is transferred by tunneling into an excited state of the adsorbed polymer. In this way, the charge-transfer process induces another equilibrium geometry in the excited molecule. The return of the electron to the metal leaves PANI-EB into another vibrational excited state than the neutral molecule leading to the emission of a Raman-shifted phonon. As a consequence, the different SERS spectrum of the PANI-EB on Au support appears as a symmetry-lowering effect produced under laser light excitation. Consequently, it is rather normal that the SERS spectrum of PANI-EB recorded on an Au substrate is similar to the SERS spectrum of the PANI-ES, the latter product being featured by a lower symmetry.

An explanation based on a possible reaction between PANI and NMP where the solvent molecules are the source of protons is less probable because, in this case, the SERS spectra should present the same variation on both metals, Au and Ag, which in reality do not occur. Besides all this, an interaction between PANI-EB and NMP molecules, as a proton source, must lead also to the appearance in the FTIR spectrum of a band at $\approx$1144 cm^{-1} evidencing a charge-transfer process. Experimental data do not confirm this.

The perturbed form induced by the reaction with the Au substrate, like the salt form, is indicated in Figure 3 by the broad Raman band peaking around 1165 cm^{-1}, which in turn discloses two components of different weight at 1162 cm^{-1} and 1172 cm^{-1}. They are associated with a C−H in-plane bending deformation for quinoid and benzoid ring, respectively.[23,25] Its upshift with increasing the SWNTs quantity in the polymerization mixture indicates a transition toward a salt structure. On the spectra S_3 of Figure 3, the final position of this band at 1175 and 1170 cm^{-1} on Ag and Au substrates, respectively, indicates less salt structure on the Au substrate. As the first sight, this result is hard to explain when an enhancement of the bands at 1330 and 1375 cm^{-1} also takes place, indicative of the salt form.[25] The variation of these two groups of bands, seemingly contradictory, become understandable if one supposes that, from the chemical synthesis, two types of composites based on PANI salt and PANI base result, each of them with a specific SERS spectrum. Similar compounds, containing both the salt and the base form of PANI, were also reported when composites were synthesized by chemical polymerization of aniline in the presence of C_{60} (ref 22). In this case, two macromolecular compounds were identified: a fullerene-doped PANI and a PANI/C_{60} composite having a “pendant chain” type structure.[22]

Furthermore, convincing evidence that the two procedures of preparation of PANI/SWNTs composite lead to different products is given by the infrared absorption spectra (Figure 4) in the FTIR spectrum of PANI-EB. The main absorption bands situated at 830, 1164, 1303, 1500, and 1590 cm^{-1} are attributed to the following vibrations: bending of C−H (out-of-plane) on benzene ring (B) p-disubstituted, bending of C−H (in-plane), vibration of the N=quinoid ring (Q)=N, stretching of $C_{aromatic}$−N, stretching of N−B−N ring, and stretching of N=Q=N ring, respectively.[26] In situ FTIR studies, concerning the protonic acid doping process of the emeraldine base, have shown that the appearance of positive charges on the macromolecular chain leads to an increase of the molecular dipole moment, which determines an increase in intensity of the absorption band at 1144 cm^{-1}. It is assigned to a vibration mode of a (B)−NH$^+$=(Q) structure.[27] In Figure 4, the curves M_1−M_3 and S_1−S_3 represent the FTIR spectra of the corresponding composite. On both groups of spectra, the presence of the absorption band at 1144 cm^{-1} demonstrate the formation of polyaniline salt whose weight in the final product increases with the nanotubes quantity. For comparison, we show also in Figure 4 spectra F_1−F_3 corresponding to PANI/C_{60} composites. They were synthesized by the chemical polymerization of aniline in the presence of C_{60}, with PANI-EB/C_{60} mass ratios of 57, 9, and 4.55, respectively. As it can be seen, a great similarity is observed between S_1−S_3 and F_1−F_3 spectra and with the absorption spectrum of polyaniline emeraldine-salt (PANI-ES). As a matter of fact, this result shows that the S composite is a PANI doped with carbon nanoparticles, namely a PANI salt.

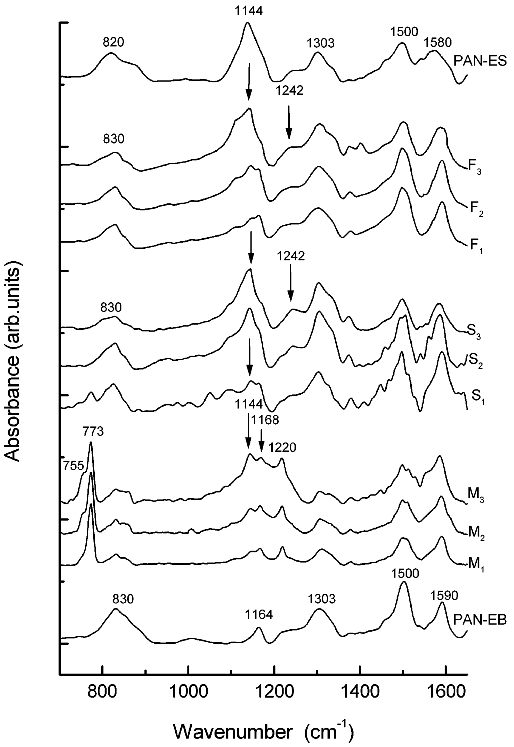

Figure 4. FTIR spectra of PANI-EB, PANI-ES, and PANI-EB/SWNTs composites obtained by mixing of compounds (spectra M_1, M_2, and M_3, respectively) and chemical synthesis (spectra S_1, S_2, and S_3, respectively). Spectra F_1, F_2, and F_3 correspond to the fullerene-doped PANI composite prepared similarly to composites of the S series.

A significant result revealed by the M spectra from Figure 4 concerns the strong absorption band at ∼773

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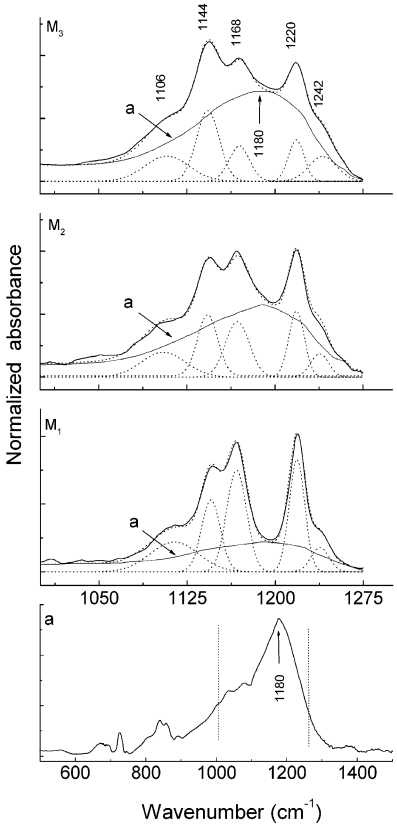

Figure 5. Deconvoluted FTIR absorption spectra of M_1, M_2, and M_3 composites. Curve a represents the absorption spectrum of carbon nanotubes.

cm^{-1} with a shoulder at ~755 cm^{-1}. They are due to the deformation of the benzoid and quinoid ring, respectively.[23] The enhancement of these bands with the increase of the nanotubes content is explainable by strong steric hindrance effects produced by the binding of voluminous particles as unbroken nanotubes or great fragments of nanotubes on the polymer chain. In this way, new covalent C−N bonds are formed between the imine nitrogen atoms of the repeating units of PANI and the carbon atoms of nanoparticles. It is worth pointing out that this steric hindrance effect is strongly related to the size of the bound particle. This explains why these bands were not observed in FTIR spectra of the F and S composites, i.e., when particles of smaller size as C_{60} or short CNT fragments with fullerenes behavior are bound to the polymer chain.

For the M composites, an analysis of the spectral range of 1000−1300 cm^{-1} is useful. Indeed, besides the band at 1144 cm^{-1}, other significant features were located at about 1106, 1168, 1180, 1220, and 1242 cm^{-1}. A large absorption band, labeled a in Figure 5, with a maximum around 1180 cm^{-1}, belongs to SWNTs (ref 16). It indicates the presence of carbon nanotubes in the M composites, as distinct absorption units. The component, with maximum at ca. 1168 cm^{-1}, is related to the polymer molecule. In fact, it is the sum of two components attributed to the C−H in-plane bending deformation for quinoid (~1162 cm^{-1}) and benzoid ring (~1172 cm^{-1}).[23] In Figure 4, one sees that for the PANI-EB, this band peaks at 1164 cm^{-1}. The charge transfer, as the main interacting process nanotube−polymer that changes the PANI structure from the base to the salt form, is spotted by the band at 1144 cm^{-1} that increases with the nanotubes content in the preparing mixture. The absorption band at ~1220 cm^{-1} attributed to C−N stretching + ring deformation (B) + C−H bending (b) vibration mode[23] is significant for the M composites. Detected as a weak band in the absorption spectrum of undoped PANI, its enhancement in M composites indicates more vibrational units associated to C−N bond achieved by the covalent bonding of the polymer on the tube surface. An appropriate microscopic picture for these composites is that of a carbon nanotube wrapped with the polymer.[28] It would explain the strong steric hindrance effects regularly observed on M-type composites based on SWNTs and other conducting polymers.[16] In Figure 5, the presence and the increase of the relative intensity of the absorption band with a maximum at ~1242 cm^{-1} has a specific meaning. Assigned to the C−N$^+$ stretching vibration in protonic acid doped PANI,[26] it indicates the formation of C−N coordinate-covalent bonds between the polymer chain and the radical cation CNT fragments. Consequently, the absorption bands situated at ~1220 and ~1242 cm^{-1} indicate two compounds, schemed in reaction 4. It contains PANI in two forms: leucoemeraldine base (PANI-LB) and emeraldine salt (PANI-ES), respectively, and their intensities ratio ($I_{1220\ \mathrm{cm}^{-1}}/I_{1242\ \mathrm{cm}^{-1}}$) becomes a measurement of the weight of the two compounds in the final product. For the M_1, M_2, and M_3 composites, the values of this ratio are 4.7, 3.0, and 1.65, respectively. The presence of two compounds in the final product is explainable if one takes into consideration the following argument. The breaking of CNTs leads to the formation of fragments of different sizes, both neutral and charged, the latter appearing as cation and anion radicals. In the case of composites from the M series, we believe that the interaction between the polymer and the nanotube or large neutral fragments involves the formation of new C−N covalent bonds that leads to polymer-functionalized carbon nanotubes. Excepting the steric hindrance effects, the covalent bonds in polyaniline-functionalized carbon nanotubes do not change the base character of the polymer. On the contrary, the interaction between the polymer and charged CNT fragments is different. It behaves as in a doping process. In this case, the formation of coordinate-covalent bonds between carbon atoms of charged CNT fragments and the amine nitrogen atoms of the repeating units of PANI will lead to a product like an emeraldine salt. It is characterized by two Raman bands[25] at ca. 1325 and 1375 cm^{-1}. However, the presented Raman spectra do not confirm a structure like this, though it must be extremely sensitive under a laser excitation at 1064 nm.[25] This fact indicates that the formation of C−N coordinative-covalent bonds involves the imine nitrogen atoms of PANI-EB, with no changes of the polymer features. A selective interaction of the CNTs with the quinoid ring of PANI was also reported for PANI/MWNTs composites[3]. A similar behavior was observed previously, studying the doping of PANI with tetrabuthylammonium tetrafloroborate $(C_4H_9)_4NBF_4$.[20] In this case, the positive charges on the macromolecular chain were obtained by the formation of the coordina-

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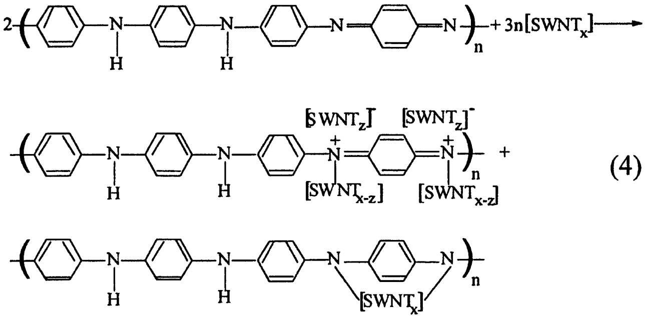
tive-covalent bonds C−N between the imine nitrogen atoms of the repeating unit of the polymer and the carbocations $C_4H_9^+$ coming from $(C_4H_9)_4NBF_4$.[20] In the case of the mixture of PANI and SWNTs, the radical anion CNT fragments compensate the positive charges induced on the polymer chain. This result is in agreement with the recently reported data concerning the chemical polymerization of aniline in the presence of SWNTs, where CNTs play the role of a doping agent.[4,29] So far, a possible instability at ambient conditions of carbon-nanotubes-doped PANI has been not reported.[4]



(4)

A composite of the type carbon nanotubes doped PANI is illustrated by the first resulted term of reaction 4. Here, we denote by [SWNT$_x$], [SWNT$_z$]$^-$, and [SWNT$_{x-z}$]$^+$ the unbroken SWNTs or neutral large fragments and fragments on the type radical anion and radical cation, with x, z, and $x-z$ corresponding to the number of carbon atoms. The last term of reaction 4 indicates a compound formed by the covalent binding of the polymer both on nanotubes with infinite length and large neutral fragments, leading to polyaniline-functionalized carbon nanotubes. In this case, the PANI is in its reduced state, i.e., of leucoemeraldine-base. This compound is difficult to detect by Raman scattering under a 1064-nm laser excitation.[25] It is well-known that PANI-leucoemeraldine base deposited on the ITO support is oxidized to the emeraldine base in a proportion of ca. 25% in 25 days.[30] This variation is observed also in the SERS spectrum of the M composites deposited on Ag support. After 7 days of storage in air, an increase of ≈18% in the intensity of the band at 1495 cm^{-1}, associated with the C=N stretching mode, is observed.

Additional studies carried out on compressed SWNTs have demonstrated the breaking of such compounds into fragments of different size, both neutral and charged, with the latter species appearing as cation and anion radicals. These fragmented nanotubes have clear signatures in their Raman spectra that can be summarized as follows: (i) a decrease of the RBM intensity, (ii) an enhancement of the D band, and (iii) the appearance of new Raman lines belonging to other graphitic particles or due to interactions between fragments. For the latter case, this is evidenced in particular by a band at ≈93 cm^{-1}. Further details will be given in a forthcoming paper.

Returning to Figures 2 and 3, we note the appearance of an additional Raman band, at about 260−270 cm^{-1}, unrelated to the metal substrate, which does not belong to polyaniline or to nanotubes. It is always stronger in the Raman spectra of S samples. Associate with $H_g(1)$ breathing vibration mode occurring in fullerenes-like particles, its presence, even in the Raman spectra of the M composites, indicates a breaking of the SWNTs and the formation of fragments of different size including precursors of closed-shell fullerenes. It puts in evidence an interaction between the polymer and the fullerene-like particles produced by the breaking of nanotubes. In this context the broad Raman band at ca. 110 cm^{-1}, equally observed on Ag and Au substrate, becomes a feature due to the intermolecular vibration modes polymer-nanotube fragments.

The stability of radical anions formed by reduction of the carbon nanoparticles involved in the salt structure of the composites may be inferred if one relates it to previous studies. For example, it is at present accepted that PANI-EB mixed with C_{60} forms a composite assimilated to fullerene-doped PANI.[31,32] It has been shown that electrons are transferred from the PANI polymer to C_{60} to form the C_{60}^- radical anion and consequently creating a positive polaron in PANI.[31−33] Raman and FTIR spectra of fullerene-doped PANI are similar to those of the emeraldine salt form (PANI-ES).[22,32] Compounds based on PANI and C_{60} produced by the chemical polymerization of the aniline in the presence of C_{60} were also reported.[33] X-ray diffractograms as well as ^{13}C NMR, FTIR, and conductivity studies conclude that these compounds behave like fullerene-doped PANI.[33] So far, the instability at ambient conditions of fullerene-doped PANI has never been reported[31−33] and our studies confirm this statement.

4. Conclusions

This paper reports new results concerning the chemical structure of PANI/SWNTs composites obtained by (i) mixing of components, i.e., the addition of dispersed SWNTs powder to the polyaniline-emeraldine base solutions, and (ii) the chemical polymerization of the aniline in the presence of SWNTs.

The main results that come out from our studies can be summarized as follows: (a) SERS and FTIR spectra of composites based on polyaniline (PANI) and single-walled carbon nanotubes (SWNTs) show strong differences with the choice of the preparation method. From the former procedure, one obtains two types of composites which contain PANI as leucoemeraldine-base and emeraldine-salt, with the structure of polymer-functionalized carbon nanotubes and nanotube-doped polymers, respectively. The other procedure of preparation, i.e., by the chemical polymerization of aniline in the presence of SWNTs, leads to composites of PANI salt behaving like a fullerene-doped PANI. These differences originate in the chemical transformation of the SWNTs in the polymerization medium ($H_2SO_4 + K_2Cr_2O_7$) of aniline, which transforms SWNTs in other particles such as graphitic particles, closed-shell fullerenes. Some of these carbon species play the role of dopant.

(b) All FTIR spectra display at 1144 cm^{-1} a growing band with the increase of the nanotubes weight in the

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preparing mixture, indicating a charge transfer between polymer and carbon nanotube.

(c) The covalent binding at the polymer chain of nanotubes or large nanotube fragments leads to a strong steric hindrance effect revealed in FTIR absorption spectra by the enhancement of complex bands at ~773 and 755 cm^{-1} assigned to the deformation of the benzoid and quinoid ring, respectively.

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